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# Monte Carlo Simulations of the Structures and Optical Absorption Spectra of $\text{AlAr}_N$ Clusters

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# Monte Carlo Simulations of the Structures and Optical Absorption Spectra of $\text{AlAr}_N$ Clusters

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## ABSTRACT

Classical Monte Carlo simulation techniques have been used in conjunction with recently devised spectral methods for constructing the ground and low-lying excited state potential energy surfaces of atomic aggregates to predict the structures and optical absorption spectra of  $\text{AlAr}_N$  clusters. The new spectral theory properly accounts for the change in electronic state character encountered in avoided crossings of diatomic adiabatic states and of the associated  $\text{AlAr}_N$  aggregate states, in contrast to strictly pairwise-additive methods such as the Balling and Wright model, which constitute special limiting cases of the general spectral theory. The  $\text{AlAr}_N$  simulations seek to understand several key issues regarding the experimental spectroscopic study of  $\text{AlAr}_N$  clusters [James M. Spotts, Chi-Kin Wong, Matthew S. Johnson, and Mitchio Okumura, *Proceedings of the HEDM Contractors' Conference*, 5-7 June 1996], such as: (1) the location of the Al atom (surface or interior), (2) the role of the 4s and 4p states of Al in the putative 3p  $\rightarrow$  3d transition, and (3) the origin of the spectral red shifts and splittings as a function of cluster size. In the case of the Al-Ar diatom, an avoided crossing between the  $\pi$  components of the 3d and 4p manifolds is expected to play a crucial role in the observed absorption spectra of  $\text{AlAr}_N$  clusters. The (17s12p5d4f)/[7s6p4d3f] atomic natural orbital basis set of Widmark et al. (supplemented with diffuse (1s1p1d1f) functions), in conjunction with internally contracted multi-reference configuration interaction (MRCI) calculations from a [6331] (3e- in 13 orbitals) state-averaged complete active space reference wavefunction, was used to calculate the Al-Ar diatomic potential energy curves which correlate with the 3p, 4s, 3d, and 4p atomic states of Al. The Ar-Ar interaction energies were computed using the "HFDB2" potential of Aziz and Slaman. Detailed comparisons are made of the calculated spectra with the available measured data.

<sup>†</sup> AFOSR University Resident Research Professor, 1997/1998.

# SPECTRAL THEORY OUTLINE

Diatomic wavefunctions written as superposition of atomic product states (direct product of Al and Ar atomic states):

$$\begin{array}{cc} \text{Al} & \text{Ar} \\ \{3P, 4S, 3D, 4P\} \otimes \{^1S_0\} \end{array}$$

$$\begin{aligned} \Phi &= \{ 3P_{+1} \bullet ^1S_0, 3P_0 \bullet ^1S_0, 3P_{-1} \bullet ^1S_0, 4S \bullet ^1S_0, 3D_{+2} \bullet ^1S_0, \dots, 4P_{-1} \bullet ^1S_0 \} \\ &= \{ 3P_{+1}, 3P_0, 3P_{-1}, 4S, 3D_{+2}, \dots, 4P_{-1} \} \end{aligned}$$

$$\Psi = \{ X \ ^2\Pi, A \ ^2\Sigma, B \ ^2\Sigma, \dots, (3) \ ^2\Pi \}$$

$$\Phi = U^t \Psi$$

Hamiltonian for atomic cluster given by:

$$H = \sum H^{(k)} + H^{(SO)}$$

$$H^{(k)} = D^t U^t E U D$$

$H^{(so)}$  = spin-orbit coupling operator for Al atom.

$E$  = diagonal matrix of diatomic interaction energies (X,A,B,C,... state energies)

$U$  = unitary matrix which transforms from the diatomic basis to the atomic-product basis.

$D$  = transformation matrix connecting the “rotated” and laboratory coordinate systems.

Atomic state mixing parameters  $U_{ij}$  obtained from eigenvectors of the diatomic and “spectral-product” transition moment matrices:  $U = U_d (U_{sp})^t$ , where  $U_d$  and  $U_{sp}$  obey the following:

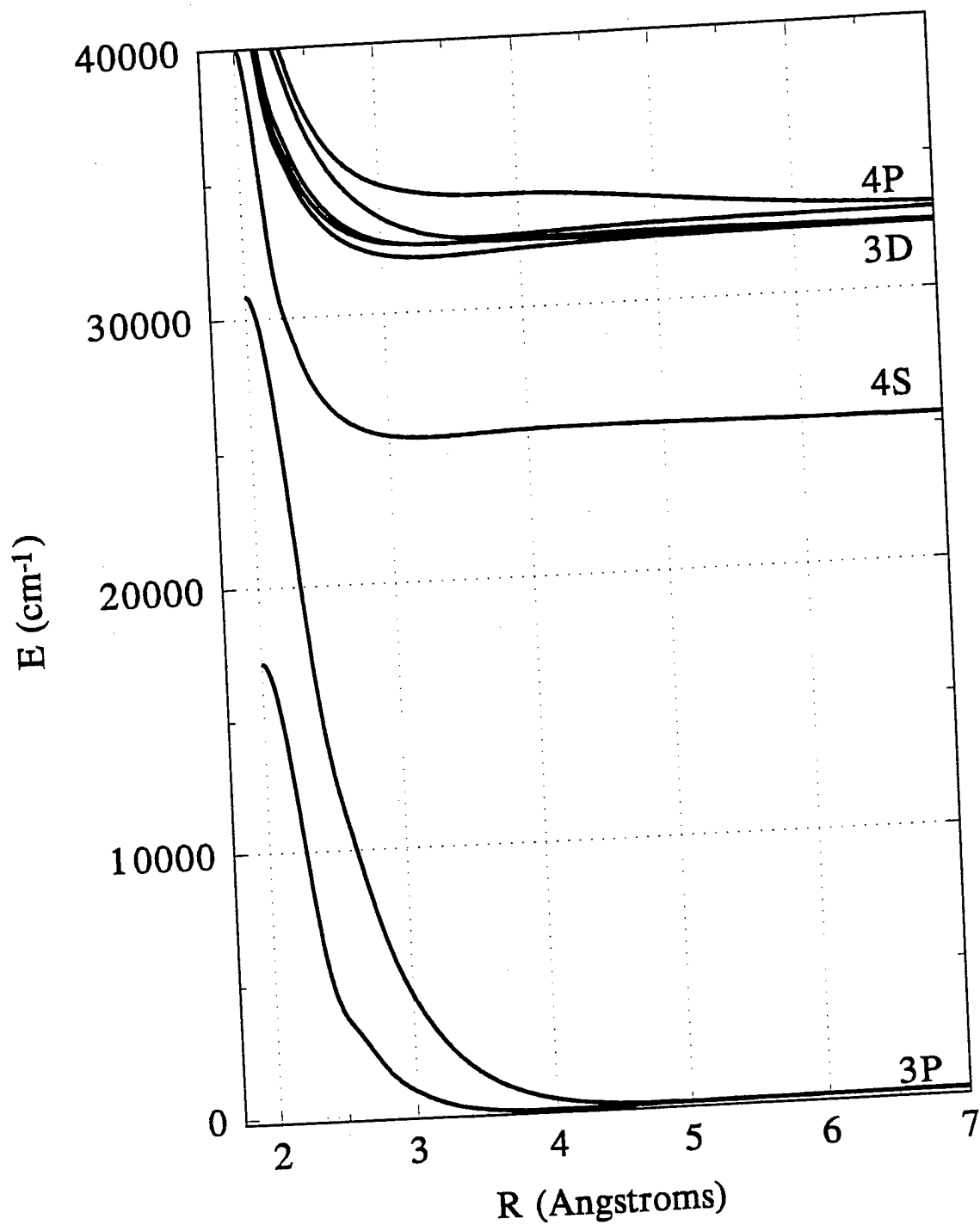
$$\lambda_d = (U_d)^t \mu(\mathbf{R}) U_d$$

and

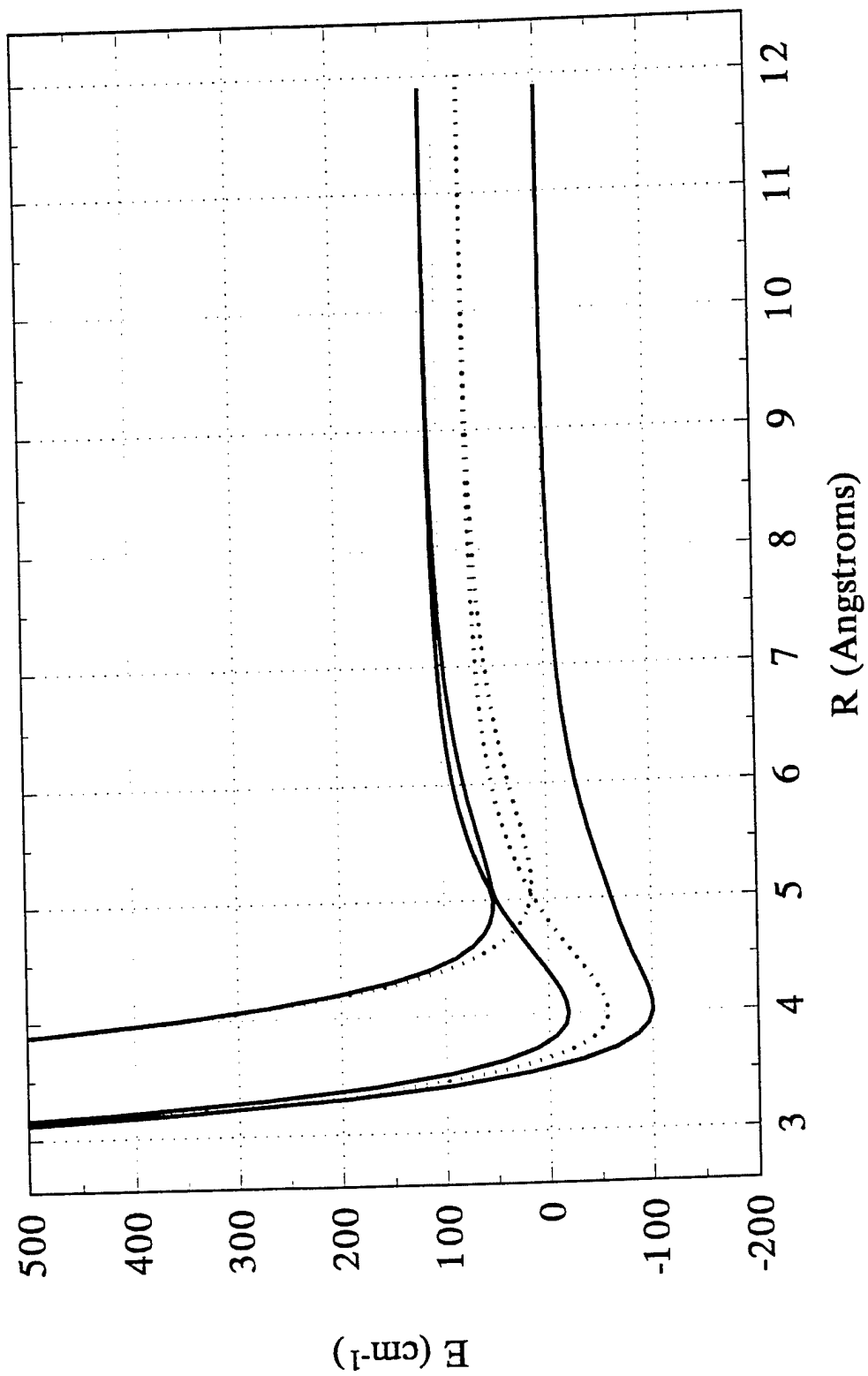
$$\lambda_{sp} = (U_{sp})^t \mu_0(\mathbf{R} \rightarrow \infty) U_{sp}$$

This is “exact” only in the case where  $\lambda_{sp} = \lambda_d$ .

# AlAr MRCI Potentials

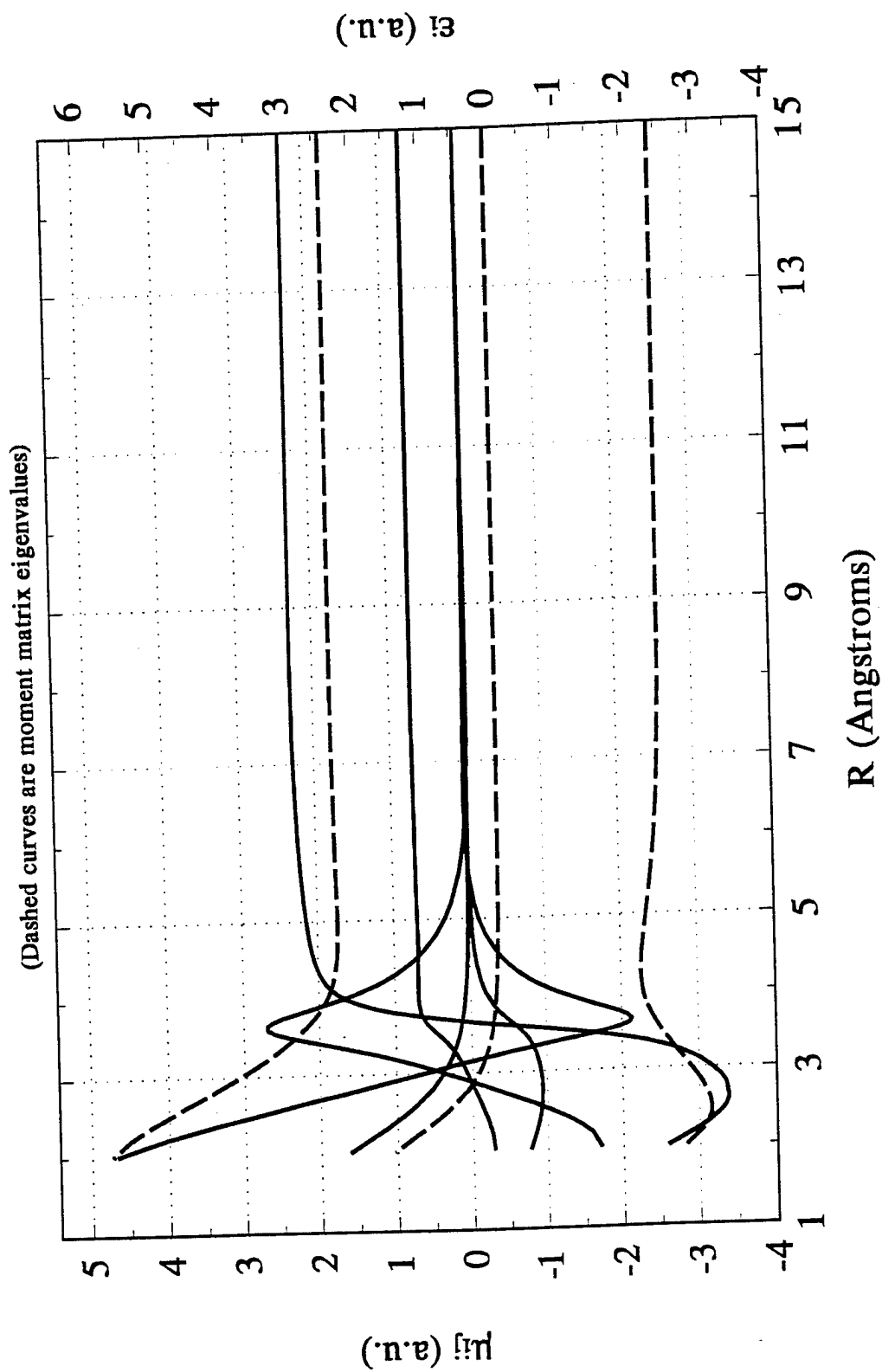


AlAr MRCI Potentials  
"3P" curves

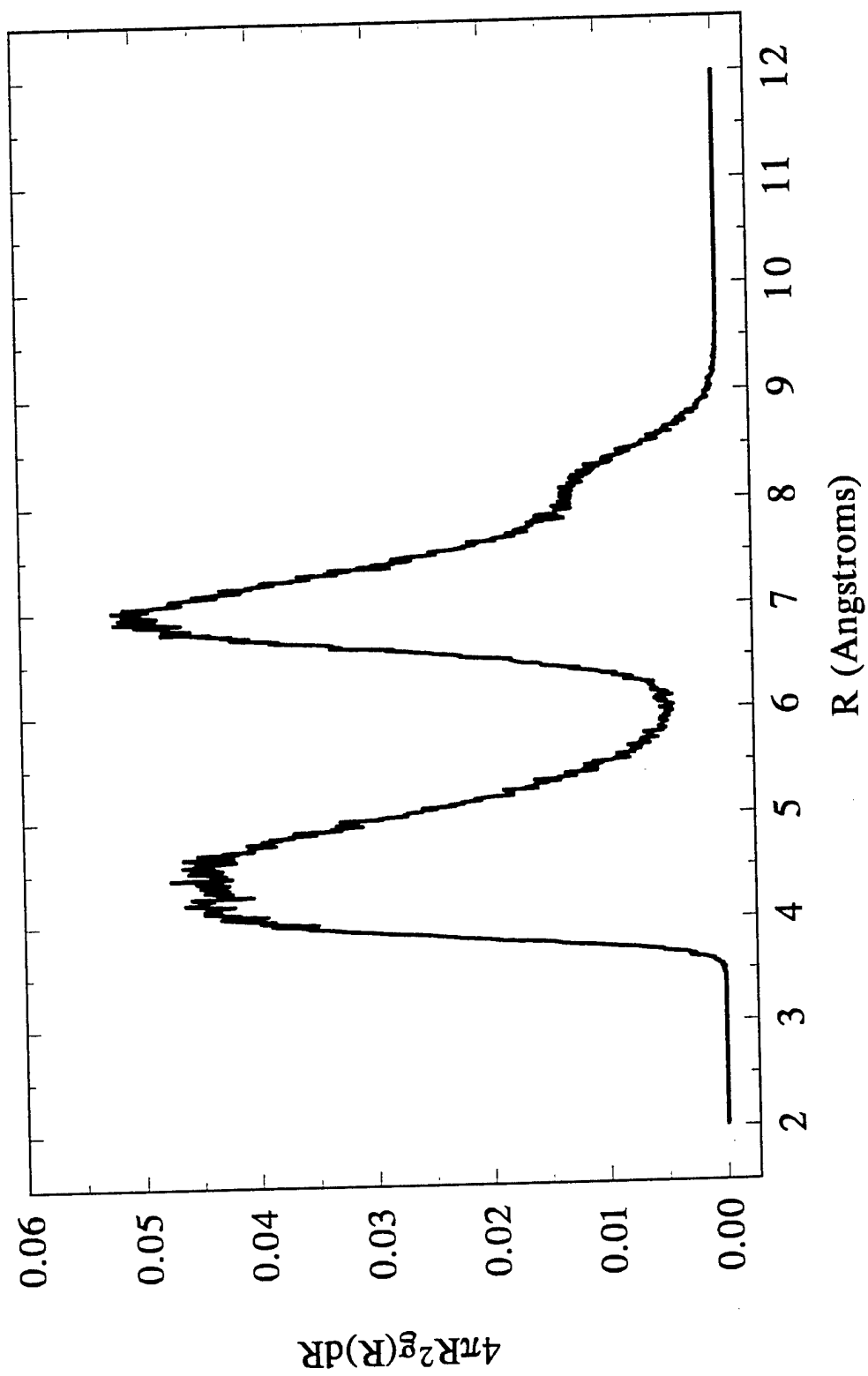




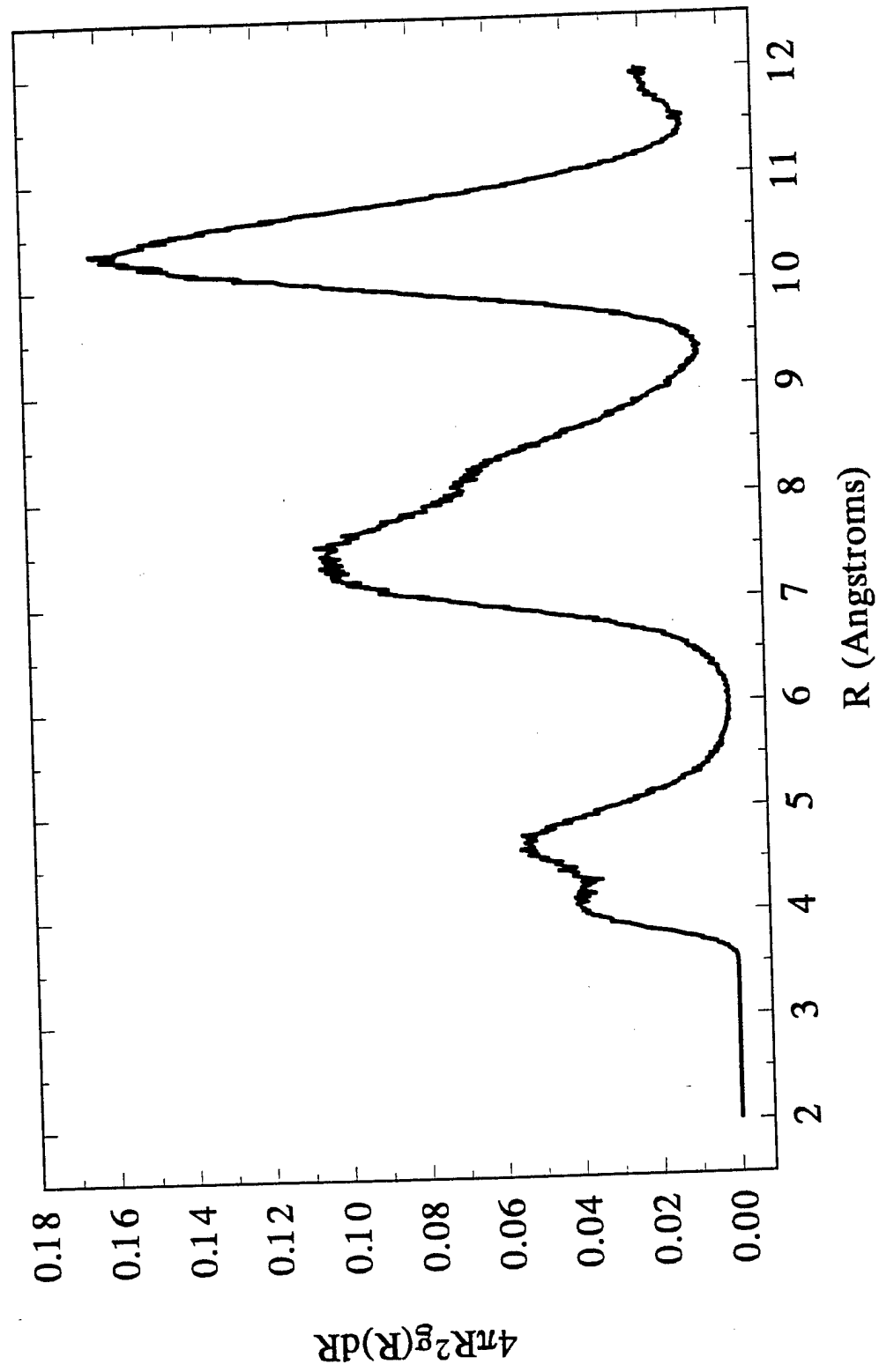
# AlAr MRCI Transition and Dipole Moments $\Pi \rightarrow \Pi$ Moments



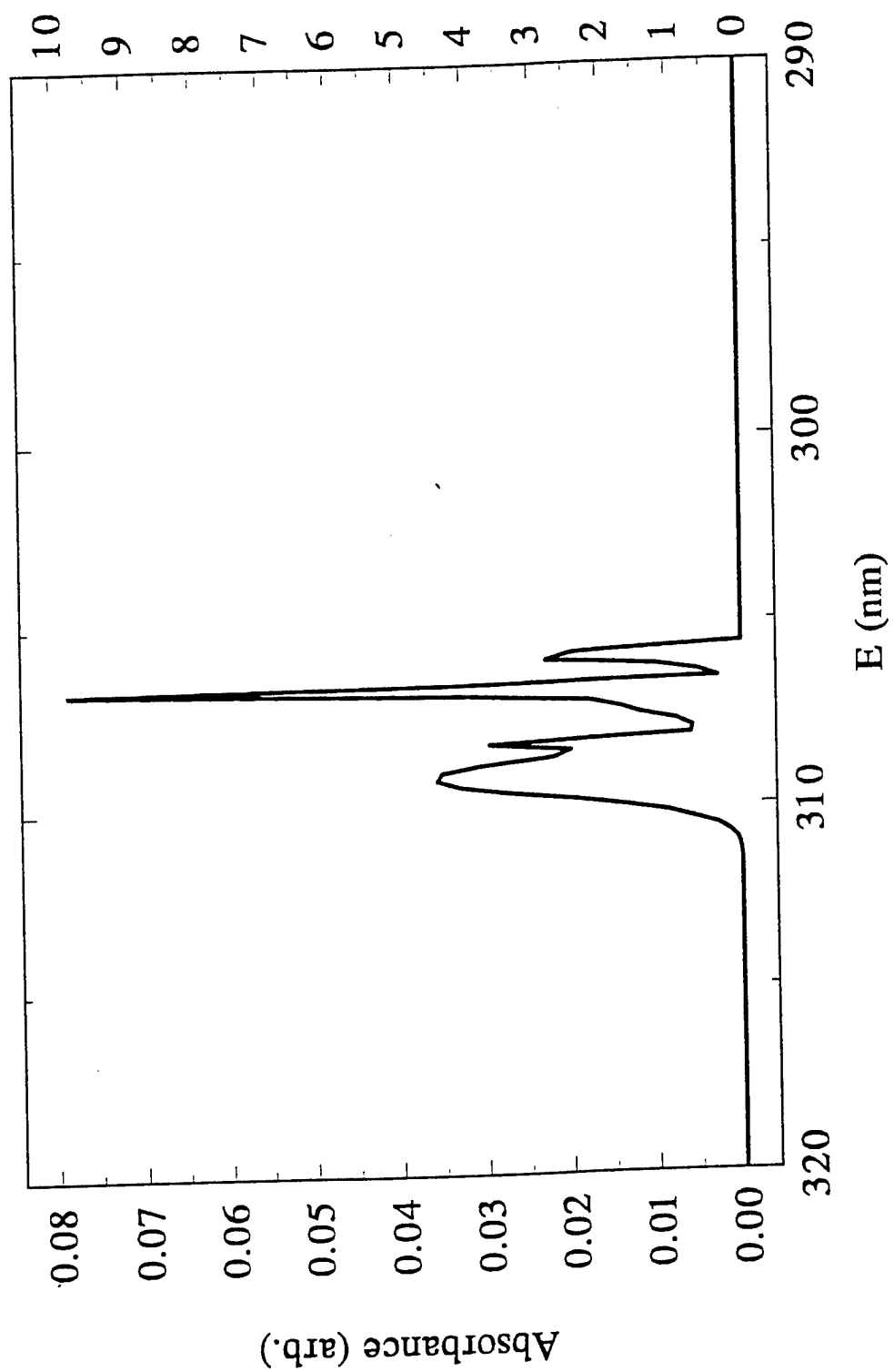
AlAr12 Radial Probability Distribution Function (RPDF)  
T = 30K



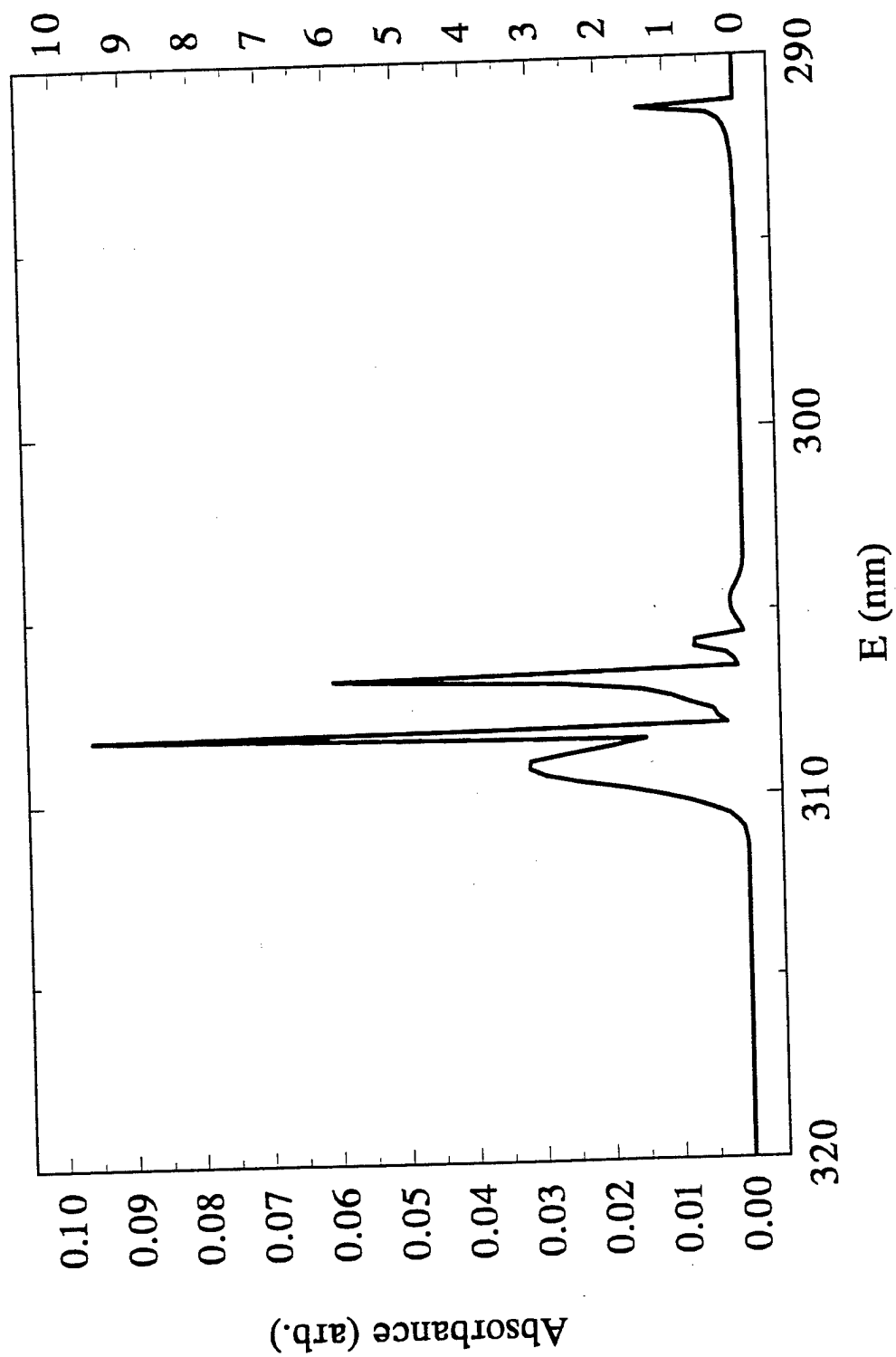
AlAr54 Radial Probability Distribution Function (RPDF)  
T = 30K



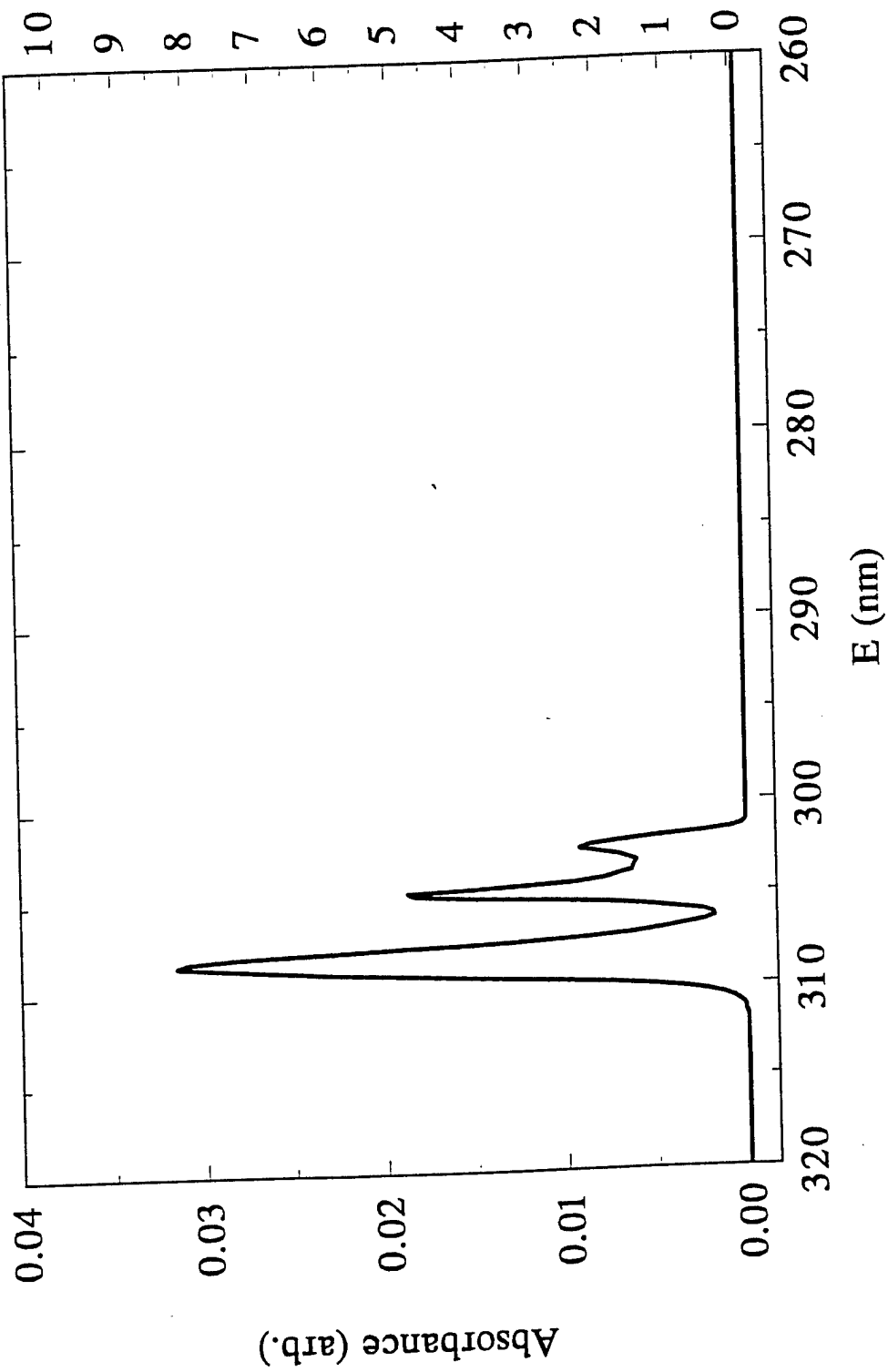
AlAr Absorption Spectrum  
T = 20K, B&W limit



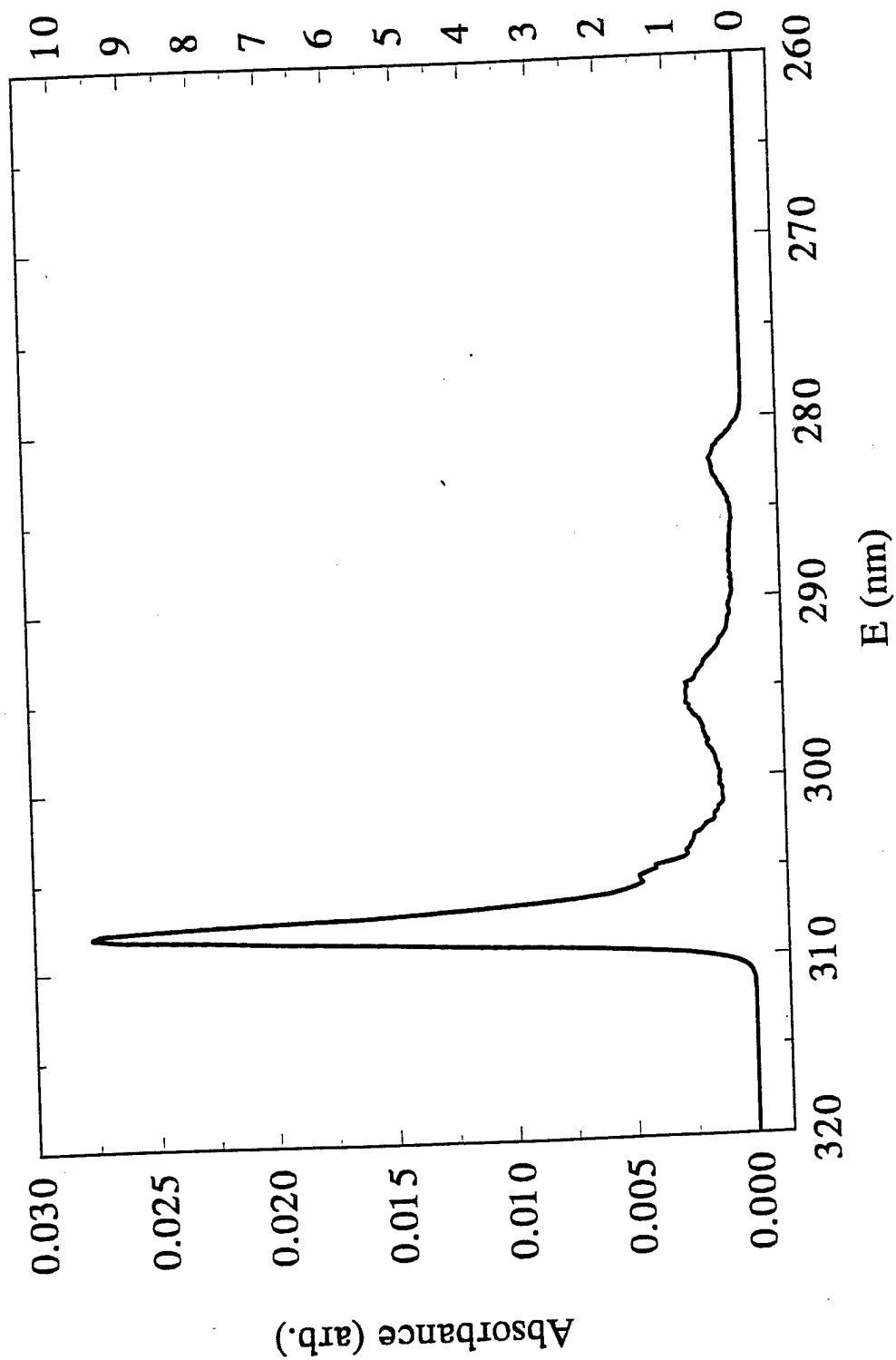
AlAr Absorption Spectrum  
T = 20K, ST



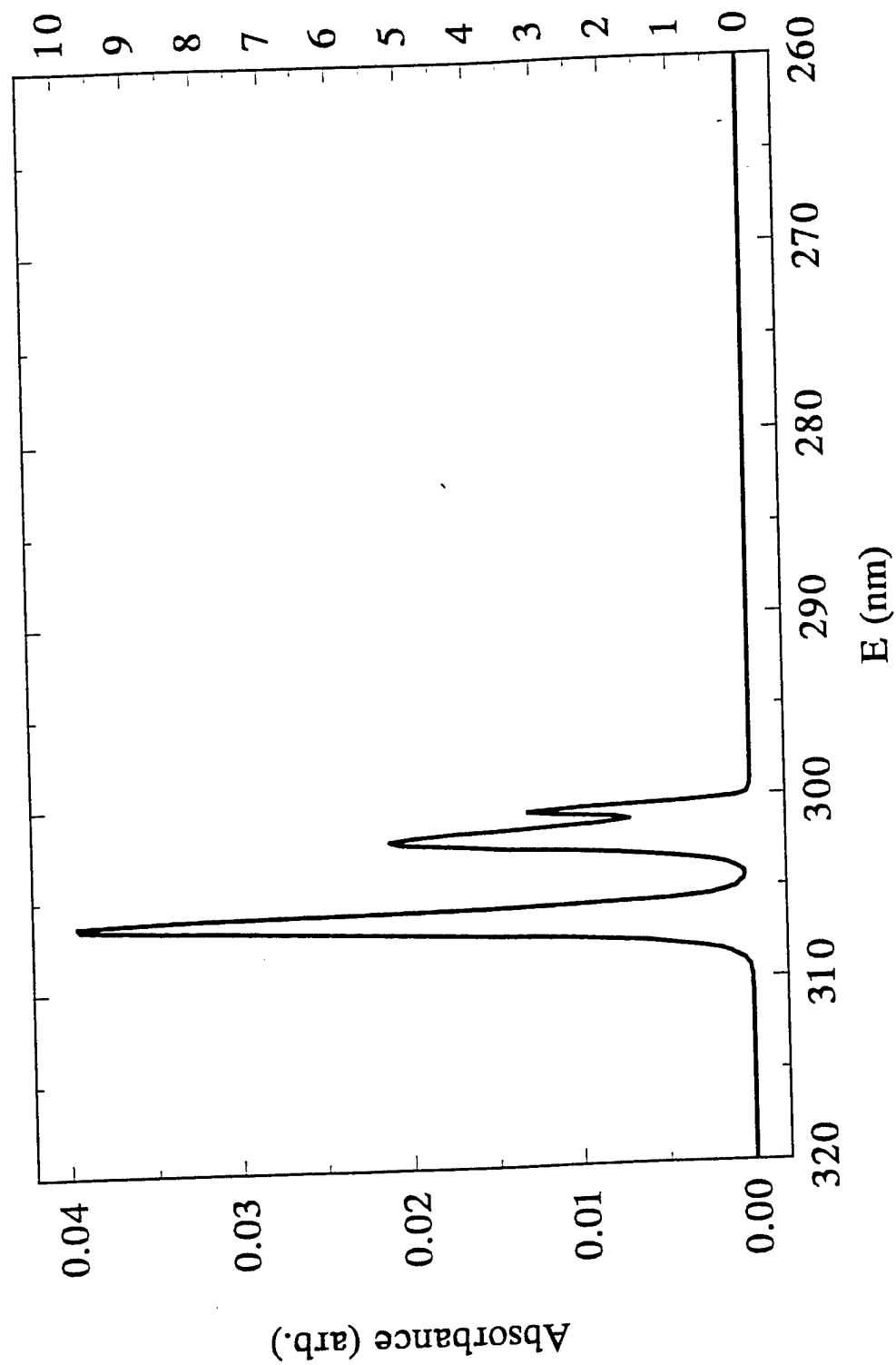
AlAr<sub>6</sub> Absorption Spectrum  
T = 30K, B&W limit



AlAr6 Absorption Spectrum  
T = 30K, ST

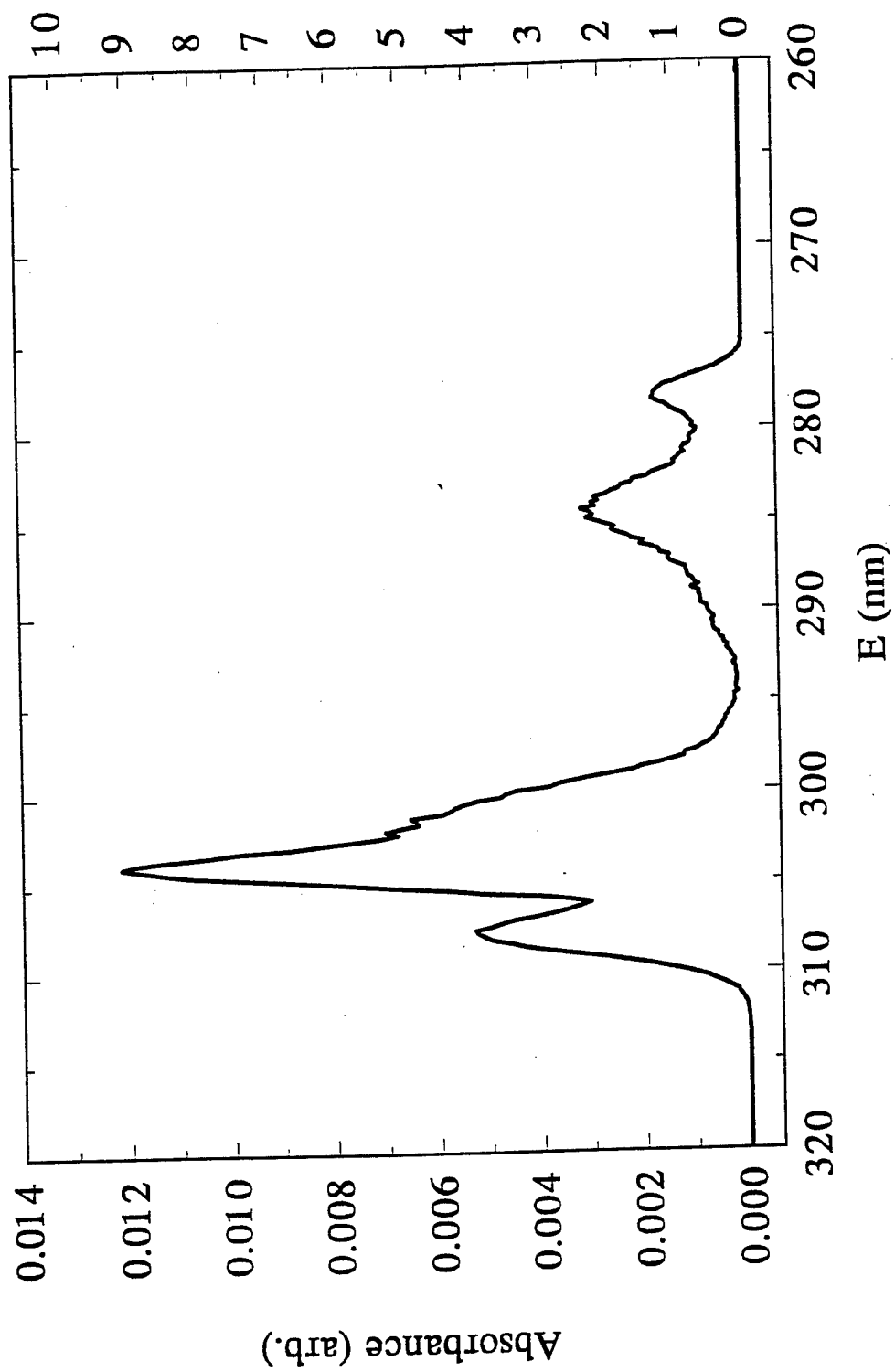


AlAr12 Absorption Spectrum  
T = 30K, B&W limit

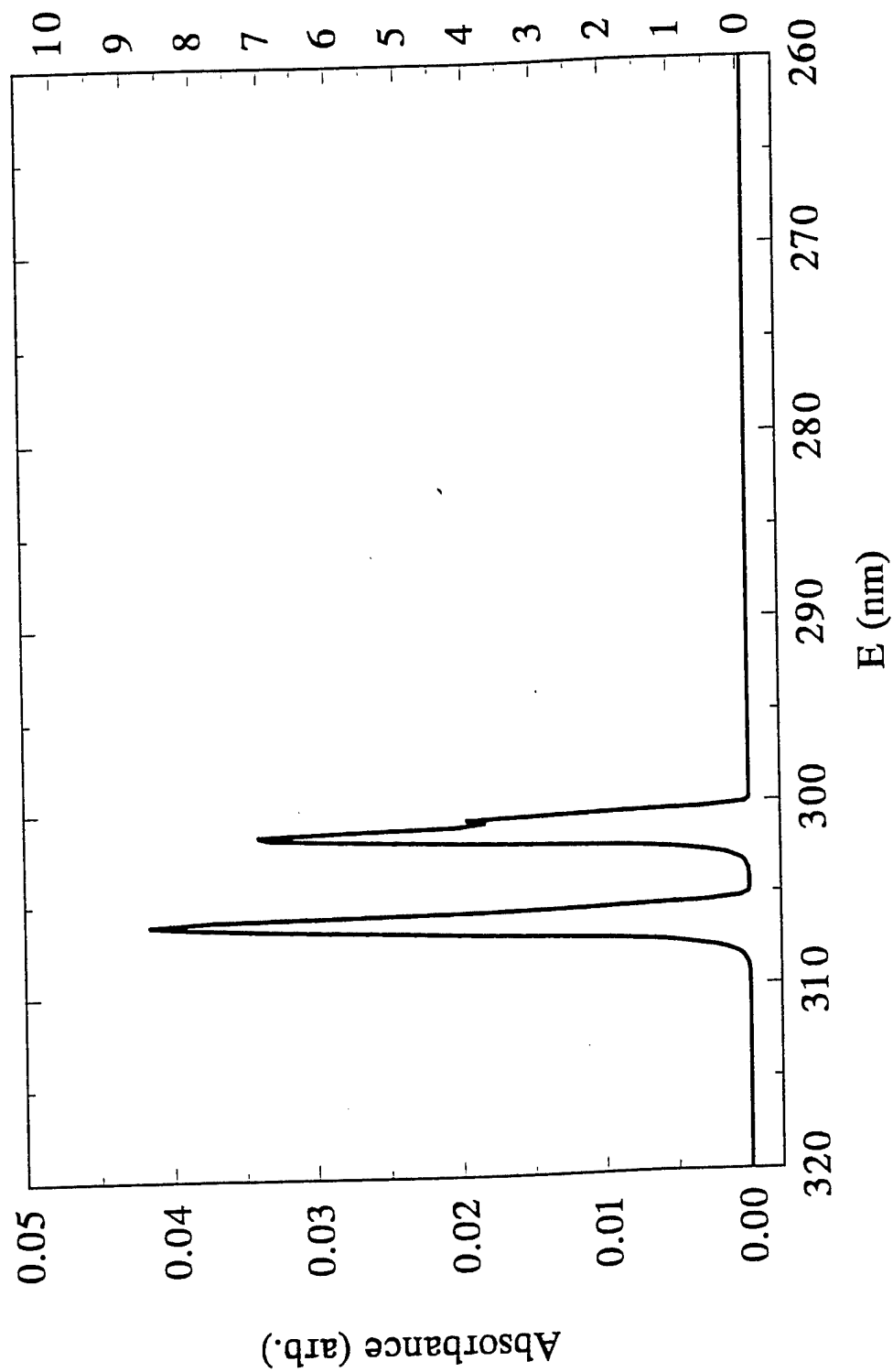




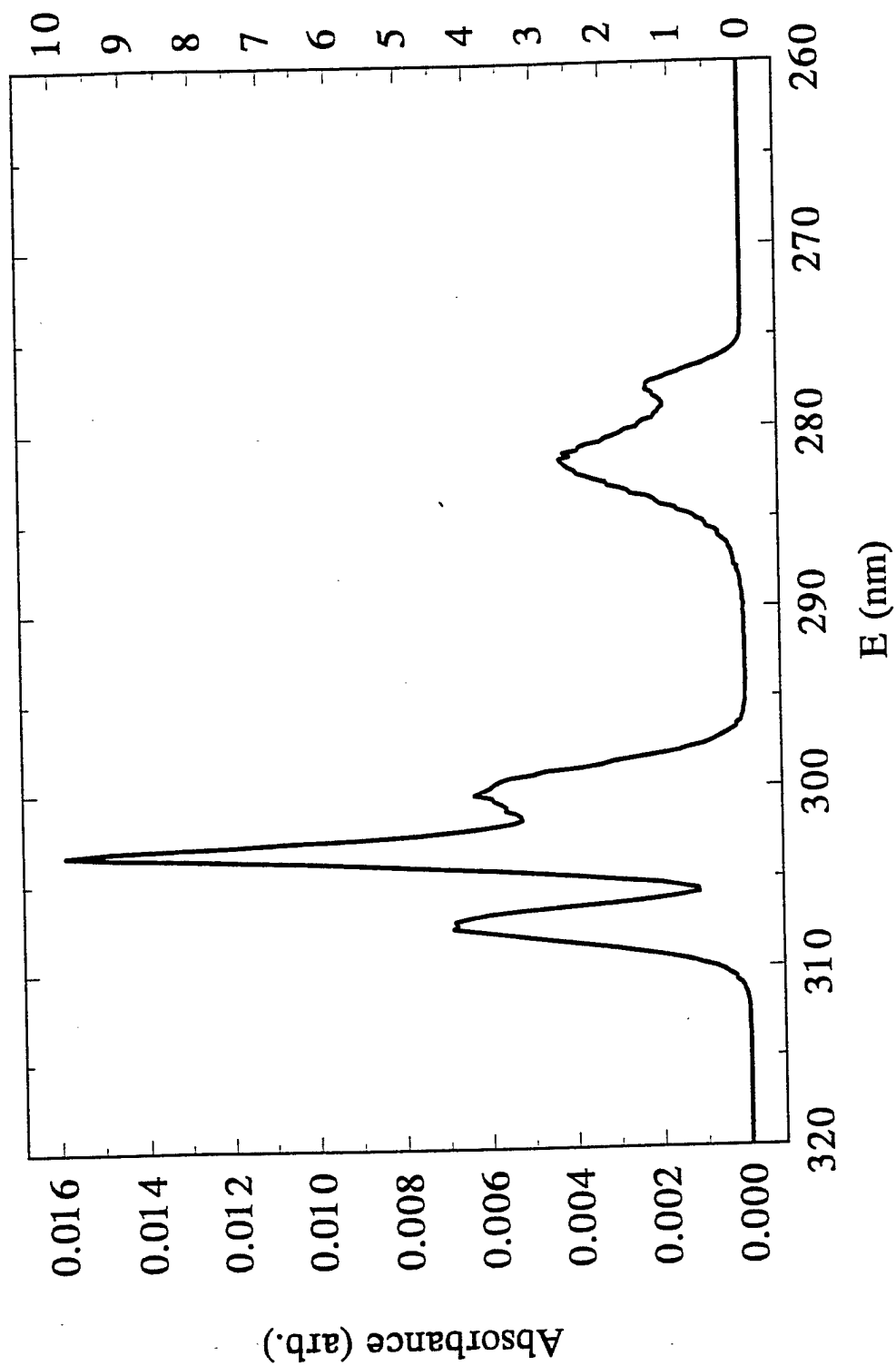
AlAr12 Absorption Spectrum  
T = 30K, ST



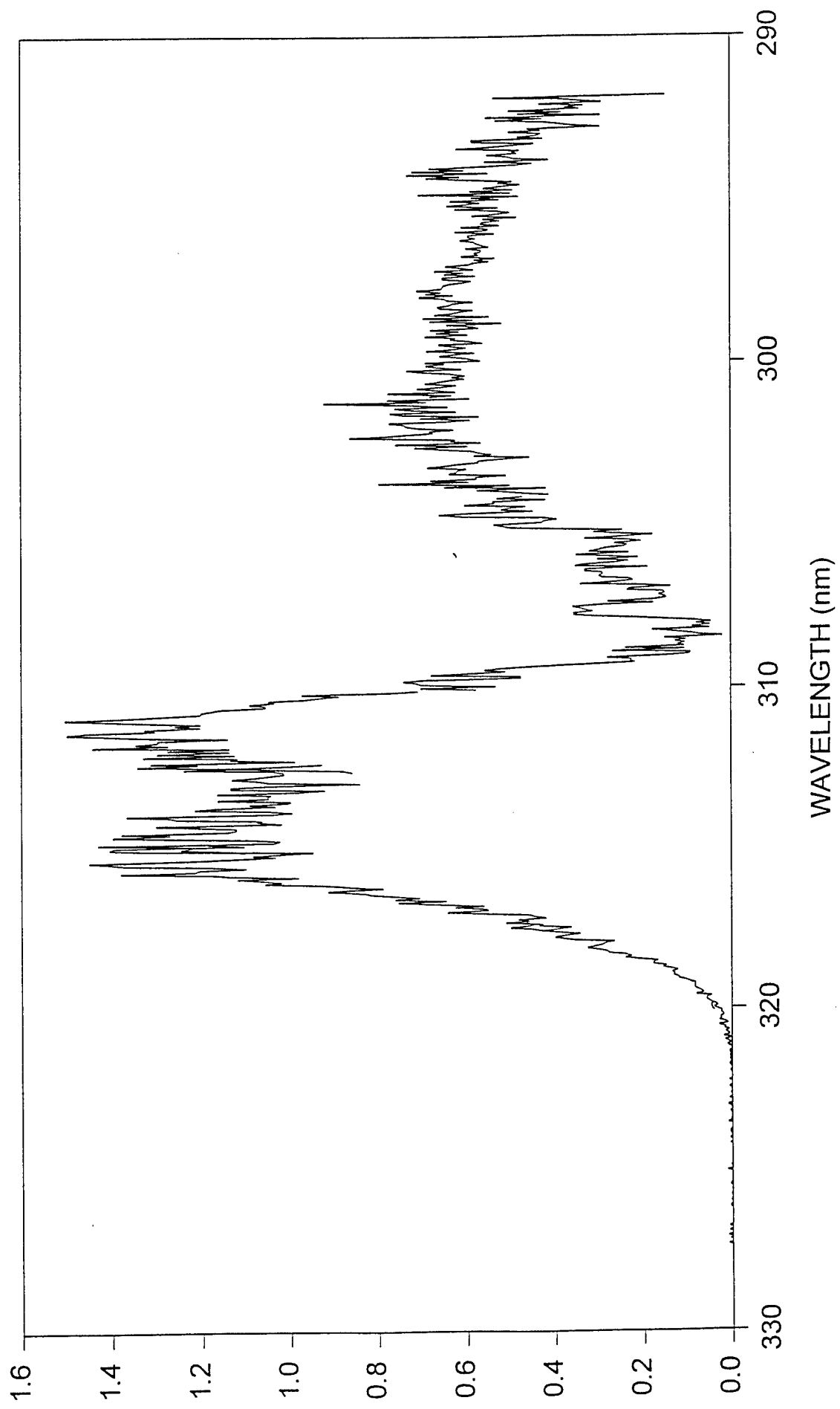
AlAr54 Absorption Spectrum  
T = 30K, B&W limit



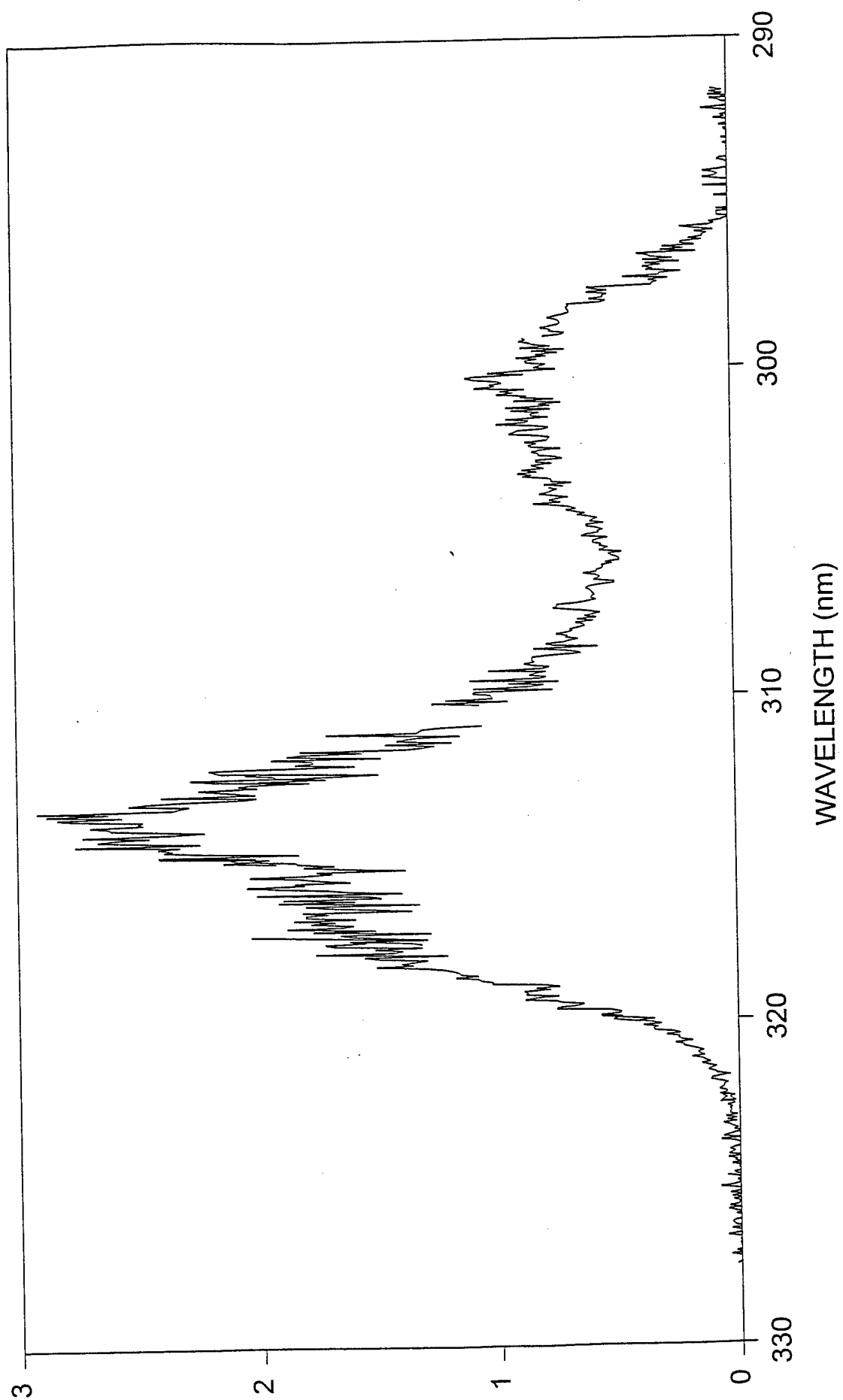
AlAr54 Absorption Spectrum  
T = 30K, ST



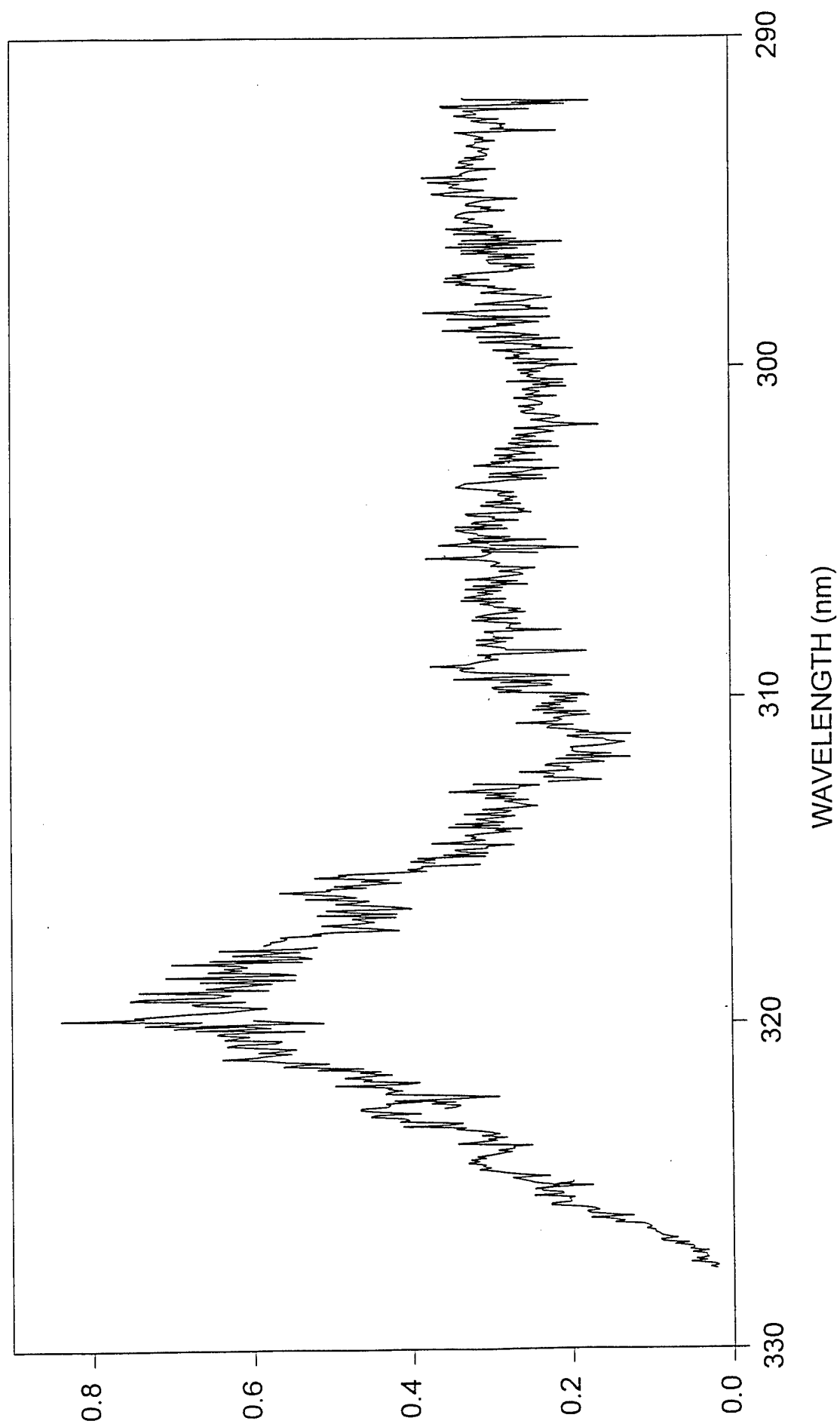
**AlAr<sub>6</sub>**



**AlAr<sub>12</sub>**



# $\text{AlAr}_{54}$



## CONCLUSIONS

1. Al is located on surface of clusters.
2. For AlAr, absorptions in the 311-306 nm range are due primarily to 3p  $\rightarrow$  3d transitions. Absorption peaks at 305 and 292 nm are due to 3d  $\rightarrow$  4p transitions.
3. In the B&W limit, the 3d-4p transitions are missing in the simulated spectra due to improper description of the avoided crossing between the 3d,4p  $\Pi$  states.
4. Simulated spectra do not reproduce observed red-shift in 3p  $\rightarrow$  3d absorptions. This may be due to missing non-additive effects in the ground state potential energy surface of the clusters.

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